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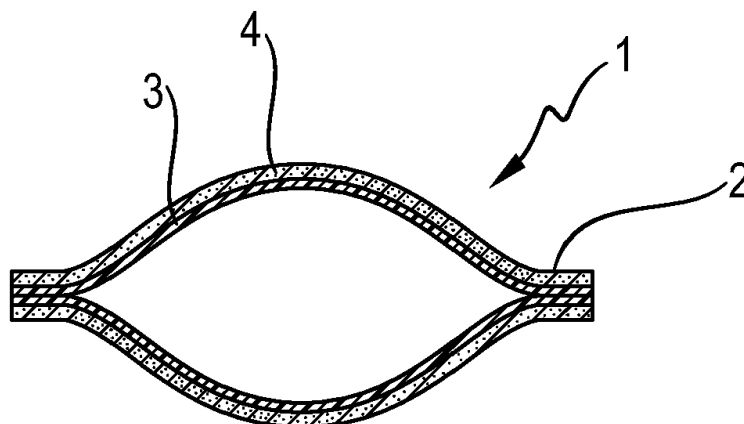
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(54) **WATER SOLUBLE UNIT DOSE DETERGENT ARTICLE COMPRISING AN AVERSIVE OR BITTERING AGENT**

(57) The present invention relates to water-soluble unit dose articles comprising multi-layer films comprising an aversive agent.

**Fig. 1**



## Description

### FIELD OF THE INVENTION

5 **[0001]** The present invention relates to water-soluble unit dose articles comprising multi-layer films comprising an aversive agent.

### BACKGROUND OF THE INVENTION

10 **[0002]** Water-soluble unit dose articles are preferred by consumers as they offer effective and efficient means of dosing appropriate levels of detergent or cleaning compositions to the wash. However, water-soluble unit dose articles come in the form of small pouches containing concentrated detergent or cleaning compositions.

**[0003]** Aversive agents can be added to water-soluble unit dose article to reduce likelihood of accidental ingestion. Such aversive agents could be substance that provide a bitter taste to the unit dose article and so elicit an instinctive impulse to spit the unit dose article out of the mouth.

15 **[0004]** There is a need to add the aversive agent in such a way that if the unit dose article is accidentally ingested, the aversive agent can effectively motivate the user to spit it out, and such effective motivation should be provided over the lifetime of the unit dose article (e.g. after a period of storage).

**[0005]** It was surprisingly found that the unit dose article of the present invention and methods of making said unit dose article overcame this problem.

### SUMMARY OF THE INVENTION

25 **[0006]** A first aspect of the present invention is a water-soluble unit dose article comprising a detergent or cleaning composition, a water-soluble film, wherein the water-soluble film comprises a first layer and a second layer wherein the first and second layers are in contact, wherein the first layer comprises a polymeric material and the second layer comprises an aversive agent.

**[0007]** A second aspect of the present invention is a process for making a water-soluble unit dose article according to any preceding claims comprising the steps of;

- 30
- a. Preparing a first layer of a water-soluble film wherein the first layer comprises polyvinyl alcohol;
  - b. Preparing a second layer of a water-soluble film wherein the second layer comprises an aversive agent;
  - c. Combining the first and second layers to form the water-soluble film;
  - d. Preparing a water-soluble unit dose article comprising the film of part c.
- 35

**[0008]** A third aspect of the present invention is a process for making a water-soluble unit dose article according to any preceding claims comprising the steps of;

- 40
- a. Preparing a first layer of a water-soluble film wherein the first layer comprises polyvinyl alcohol;
  - b. Adding a second layer onto the first layer, wherein the second layer comprises an aversive agent by adding the second layer via coating, spraying, printing, electrostatic transfer and mixtures thereof to form the water-soluble film;
  - c. Preparing a water-soluble unit dose article comprising the film of part b.

45 **[0009]** A fourth aspect of the present invention is a process for making a water-soluble unit dose article according to any preceding claims comprising the steps of;

- 50
- a. Preparing a water-soluble unit dose article comprising a film having a first layer, wherein the first layer comprises polyvinyl alcohol;
  - b. Adding a second layer onto the first layer, wherein the second layer comprises an aversive agent by adding the second layer via coating, spraying, printing, electrostatic transfer and mixtures thereof.

### BRIEF DESCRIPTION OF THE DRAWINGS

#### **[0010]**

55 Fig. 1 shows a side profile cross section of a water-soluble unit dose article comprising a film having a first layer and a second layer, wherein the second layer comprises an aversive agent.

Fig.2 shows a unit dose article comprising a film having a first layer and a second layer wherein the second layer is present as a discrete region on the surface of the first layer and wherein the second layer comprises an aversive agent.

## DETAILED DESCRIPTION OF THE INVENTION

### Water-soluble unit dose article

**[0011]** The present invention is to a water-soluble unit dose article comprising a detergent or cleaning composition, a water-soluble film, wherein the water-soluble film comprises a first layer and a second layer wherein the first and second layers are in contact, wherein the first layer comprises polyvinyl alcohol and the second layer comprises an aversive agent.

**[0012]** The water-soluble unit dose article comprises at least one water-soluble film shaped such that the unit-dose article comprises at least one internal compartment surrounded by the water-soluble film. The at least one compartment comprises the detergent or cleaning composition. The water-soluble film is sealed such that the detergent or cleaning composition does not leak out of the compartment during storage. However, upon addition of the water-soluble unit dose article to water, the water-soluble film dissolves and releases the contents of the internal compartment into the wash liquor.

**[0013]** The compartment should be understood as meaning a closed internal space within the unit dose article, which holds the composition. Preferably, the unit dose article comprises a water-soluble film. The unit dose article is manufactured such that the water-soluble film completely surrounds the composition and in doing so defines the compartment in which the composition resides. The unit dose article may comprise two films. A first film may be shaped to comprise an open compartment into which the composition is added. A second film is then laid over the first film in such an orientation as to close the opening of the compartment. The first and second films are then sealed together along a seal region. The film is described in more detail below.

**[0014]** The unit dose article may comprise more than one compartment, even at least two compartments, or even at least three compartments. The compartments may be arranged in superposed orientation, i.e. one positioned on top of the other. Alternatively, the compartments may be positioned in a side-by-side orientation, i.e. one orientated next to the other. The compartments may even be orientated in a 'tyre and rim' arrangement, i.e. a first compartment is positioned next to a second compartment, but the first compartment at least partially surrounds the second compartment, but does not completely enclose the second compartment. Alternatively one compartment may be completely enclosed within another compartment.

**[0015]** Wherein the unit dose article comprises at least two compartments, one of the compartments may be smaller than the other compartment. Wherein the unit dose article comprises at least three compartments, two of the compartments may be smaller than the third compartment, and preferably the smaller compartments are superposed on the larger compartment. The superposed compartments preferably are orientated side-by-side.

**[0016]** In a multi-compartment orientation, the composition according to the present invention may be comprised in at least one of the compartments. It may for example be comprised in just one compartment, or maybe comprised in two compartments, or even in three compartments.

**[0017]** Each compartment may comprise the same or different compositions. The different compositions could all be in the same form, for example they may all be liquid, or they may be in different forms, for example one or more may be liquid and one or more may be solid.

**[0018]** The detergent or cleaning composition may be present in one compartment or may be present in more than one compartment.

**[0019]** The water-soluble unit dose article comprises a detergent or cleaning composition. Detergent or cleaning compositions are described in more detail below.

**[0020]** The water-soluble unit dose article comprises a water-soluble film, wherein the water-soluble film comprises a first layer and a second layer. Water-soluble films are described in more detail below. The second layer comprises an aversive agent. Aversive agents are described in more detail below.

**[0021]** The water-soluble unit dose article may comprise an air bubble.

**[0022]** The water-soluble unit dose article may be transparent, translucent or opaque.

**[0023]** Preferably, at least 5%, or even at least 10%, or even at least 20%, or even at least 30% of the aversive agent is lost from the unit dose article with 20 seconds following contact of the unit dose article with an artificial saliva solution. Those skilled in the art will know how to formulate an artificial saliva solution or know where to source one commercially.

### Water-soluble film

**[0024]** The water-soluble film comprises a first layer and a second layer wherein the first and second layers are in contact, wherein the first layer comprises a polymeric material and the second layer comprises an aversive agent.

**[0025]** It should be understood that the detergent composition is not located between the first and second layers. The

film comprising the first and second layers is arranged so as to define an inner compartment wherein the detergent resides. However, the inner compartment is not defined between the first and second layer. Rather the film as a whole, comprising the first and second layers should be understood as defining the compartment in which the detergent resides. The unit dose article may comprise two films, wherein at least one of the films comprises a first layer and second layer according to the present invention and wherein the first and second films define the inner compartment in which the detergent resides.

**[0026]** Preferably, the water-soluble film comprises between 5mg/m<sup>2</sup> and 500mg/m<sup>2</sup>, preferably between 20mg/m<sup>2</sup> and 200 mg/m<sup>2</sup> of the water-soluble film of the aversive agent. More preferably, the second layer comprises between 5mg/m<sup>2</sup> and 500mg/m<sup>2</sup>, preferably between 20mg/m<sup>2</sup> and 200 mg/m<sup>2</sup> of the water-soluble film of the aversive agent. By 'mg/m<sup>2</sup>' we herein mean that for any particular portion of film wherein that film has a surface area of 1m<sup>2</sup>, that portion of film comprises between 5mg and 500mg of aversive agent. Wherein a single layer alone comprises between 5 mg/m<sup>2</sup> and 500mg/m<sup>2</sup> aversive agent, we herein mean that any particular portion of that layer that has a surface area of 1m<sup>2</sup> comprising between 5mg and 500mg of aversive agent. Preferably, for any particular portion of film prior to said film being deformed in any way through e.g. thermoforming, wherein that film has a surface area of 1m<sup>2</sup>, that portion of film prior to being deformed comprises between 5mg and 500mg of aversive agent. The aversive agent is described below.

**[0027]** The first and second layers are in contact. The first layer has an inner surface and an outer surface. The second layer is in contact with at least a portion of one of the surfaces of the first layer, or is in contact with an entire surface of the first layer. Preferably the second layer is in contact with at least a portion of the outer surface of the first layer or the entire outer surface of the first layer. Herein we mean that the inner surface of the first layer is the surface that is in contact with, or facing the detergent or cleaning composition held within the unit dose article. The outer surface of the first layer is the surface that is directly opposite to the inner surface.

**[0028]** The second layer may be in contact with between 5% and 100%, preferably between 10% and 95%, more preferably between 15% and 90% of the surface area of either the inner surface or the outer surface of the first layer.

**[0029]** The second layer may be arranged in one or more discrete regions on the outer surface of the first layer or may be homogeneously distributed across the whole outer surface of the first layer. For example the outer surface of the first layer may comprise regions comprising the second layer and regions purposively devoid of the second layer. By homogeneously distributed we mean that the second layer is distributed across the entire outer surface of the first layer but the homogenous distribution may result in regions of higher concentration than others. However, homogeneously distributed means that no area of the outer surface of the first layer has intentionally been left devoid of the second layer.

The first and second layers are described in more detail below.

**[0030]** The water-soluble unit dose article may comprise an area of print. The water-soluble unit dose article may be printed using flexographic techniques, ink jet printing techniques or a mixture thereof. The printed area may be on the film, preferably on the outside of the film, within the film, on the inside of the film or a mixture thereof. The printed area may convey information such as usage instructions, chemical safety instructions or a mixture thereof. Alternatively, the entire surface of the pouch, or substantially the entire surface of the pouch is printed in order to make the pouch opaque. The print may convey an image that reduces the risk of confusion and hence accidental ingestion of the pouch.

**[0031]** Preferably the water-soluble film is one that exhibits at least a 50% aversive retention of at least 2 weeks, preferably at least 4 weeks, more preferably at least 1 month, most preferably at least 2 months. By 'aversive retention' we herein mean at least 50% of the initial concentration of aversive agent added to the water-soluble film remains in the water-soluble film after at least 2 weeks, preferably at least 4 weeks, more preferably at least 1 month, most preferably at least 2 months.

#### First layer

**[0032]** The first layer is soluble or dispersible in water.

**[0033]** Preferably the first layer is one that exhibits at least a 50% aversive retention of at least 2 weeks, preferably at least 4 weeks, more preferably at least 1 month, most preferably at least 2 months. By 'aversive retention' we herein mean at least 50% of the initial concentration of aversive agent added to the first layer remains in the first layer after at least 2 weeks, preferably at least 4 weeks, more preferably at least 1 month, most preferably at least 2 months.

**[0034]** The first layer preferably has a thickness of from 20 to 200 microns, preferably 35 to 150 microns, even more preferably 50 to 125 microns, most preferably from 75 to 100 microns, or 76 microns, or 100 microns. Preferably, the first layer prior to being made into a water-soluble unit dose article has a thickness between 20μm and 200μm, preferably between 35μm and 150μm, even more preferably between 50μm and 125μm, most preferably between 75μm and 100μm or 76 microns, or 100 microns. Herein we mean the thickness of the first layer before it has been subjected to any thermoforming, elastic strain or plasticization techniques such as thermoforming into a mould for example or stretching from general film handling.

**[0035]** Different film material and/or films of different thickness may be employed in making the compartments of the present invention. A benefit in selecting different films is that the resulting compartments may exhibit different solubility

or release characteristics.

**[0036]** Preferred films for the first layer exhibit good dissolution in cold water, meaning unheated distilled water. Preferably such films exhibit good dissolution at temperatures 24°C, even more preferably at 10°C. By good dissolution it is meant that the film exhibits water-solubility of at least 50%, preferably at least 75% or even at least 95%, as measured, by the method set out here after using a glass-filter with a maximum pore size of 20 microns, described below. Water-solubility may be determined at 24°C, or preferably at 10°C. Dissolution Method: 50 grams  $\pm$  0.1 gram of film material is added in a pre-weighed 400 ml beaker and 245ml  $\pm$  1 ml of distilled water is added. This is stirred vigorously on a magnetic stirrer, labline model No. 1250 or equivalent and 5 cm magnetic stirrer, set at 600 rpm, for 30 minutes at 24°C. Then, the mixture is filtered through a folded qualitative sintered-glass filter with a pore size as defined above (max. 20 micron). The water is dried off from the collected filtrate by any conventional method, and the weight of the remaining material is determined (which is the dissolved or dispersed fraction). Then, the percentage solubility or dispersability can be calculated.

**[0037]** The first layer comprises a polymeric material. The first layer can, for example, be obtained by casting, blow-moulding, extrusion, or blown extrusion of the polymeric material, as known in the art. Preferably the first layer is obtained by an extrusion process or by a casting process.

**[0038]** Preferred polymers for the first layer (including copolymers, terpolymers, or derivatives thereof) suitable for use as film material are selected from polyvinyl alcohols (PVA), polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts, polyaminoacids or peptides, polyamides, polyacrylamide, copolymers of maleic/acrylic acids, polysaccharides including starch and gelatine, natural gums such as xanthum and carragum. More preferred polymers are selected from polyacrylates and water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose sodium, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltodextrin, polymethacrylates, and most preferably selected from polyvinyl alcohols, polyvinyl alcohol copolymers and hydroxypropyl methyl cellulose (HPMC), and combinations thereof. Preferably, the polymers of the film material are free of carboxylate groups.

**[0039]** Preferably, the level of polymer in the first layer, for example a PVA polymer, is at least 60%. The polymer can have any weight average molecular weight, preferably from about 1000 to 1,000,000, more preferably from about 10,000 to 300,000, yet more preferably from about 20,000 to 150,000.

**[0040]** Mixtures of polymers can also be used as the film material for the first layer. This can be beneficial to control the mechanical and/or dissolution properties of the compartments or pouch, depending on the application thereof and the required needs. Suitable mixtures include for example mixtures wherein one polymer has a higher water-solubility than another polymer, and/or one polymer has a higher mechanical strength than another polymer. Also suitable are mixtures of polymers having different weight average molecular weights, for example a mixture of PVA or a copolymer thereof of a weight average molecular weight of about 10,000 to about 40,000, preferably about 20,000, and of PVA or copolymer thereof, with a weight average molecular weight of about 100,000 to about 300,000, preferably about 150,000. Also suitable herein are polymer blend compositions, for example comprising hydrolytically degradable and water-soluble polymer blends such as polylactide and polyvinyl alcohol, obtained by mixing polylactide and polyvinyl alcohol, typically comprising about 1-35% by weight polylactide and about 65% to 99% by weight polyvinyl alcohol. Preferred for use herein are polymers, preferably polyvinyl alcohol, which are from about 60% to about 99% hydrolysed, preferably from about 80% to about 99% hydrolysed, even more preferably from about 80% to about 90% hydrolysed, to improve the dissolution characteristics of the material. Preferred films are those supplied by Monosol (Merrillville, Indiana, USA) under the trade references M8630, M8900, M8779, M8310, M9467, and PVA films of corresponding solubility and deformability characteristics. Other suitable films may include called Solublon® PT, Solublon® GA, Solublon® KC or Solublon® KL from the Aicello Chemical Europe GmbH, the films VF-HP by Kuraray, or the films by Nippon Gohsei, such as Hi Selon. Suitable films for the first layer include those supplied by Monosol for use in the following Procter and Gamble products: TIDE PODS, CASCADE ACTION PACS, CASCADE PLATINUM, CASCADE COMPLETE, ARIEL 3 IN 1 PODS, TIDE BOOST ORIGINAL DUO PACs, TIDE BOOST FEBREZE SPORT DUO PACS, TIDE BOOST VIVID WHITE BRIGHT PACS, DASH, FAIRY PLATINUM. It may be preferable to use a film for the first layer that exhibits better dissolution than M8630 film, supplied by Monosol, at temperatures 24°C, even more preferably at 10°C.

**[0041]** Preferred water soluble films for the first layer are those derived from a resin that comprises a blend of polymers, preferably wherein at least one polymer in the blend is polyvinyl alcohol. Preferably, the water soluble film resin in the first layer comprises a blend of PVA polymers. For example, the PVA resin can include at least two PVA polymers, wherein as used herein the first PVA polymer has a viscosity less than the second PVA polymer. A first PVA polymer can have a viscosity of at least 8 centipoise (cP), 10 cP, 12 cP, or 13 cP and at most 40 cP, 20 cP, 15 cP, or 13 cP, for example in a range of about 8 cP to about 40 cP, or 10 cP to about 20 cP, or about 10 cP to about 15 cP, or about 12 cP to about 14 cP, or 13 cP. Furthermore, a second PVA polymer can have a viscosity of at least about 10 cP, 20 cP, or 22 cP and at most about 40 cP, 30 cP, 25 cP, or 24 cP, for example in a range of about 10 cP to about 40 cP, or 20 to about 30 cP, or about 20 to about 25 cP, or about 22 to about 24, or about 23 cP. The viscosity of a PVA polymer is determined by measuring a freshly made solution using a Brookfield LV type viscometer with UL adapter as described

in British Standard EN ISO 15023-2:2006 Annex E Brookfield Test method. It is international practice to state the viscosity of 4% aqueous polyvinyl alcohol solutions at 20°C. All viscosities specified herein in cP should be understood to refer to the viscosity of 4% aqueous polyvinyl alcohol solution at 20 °C, unless specified otherwise. Similarly, when a resin is described as having (or not having) a particular viscosity, unless specified otherwise, it is intended that the specified

viscosity is the average viscosity for the resin, which inherently has a corresponding molecular weight distribution.

**[0042]** The individual PVA polymers can have any suitable degree of hydrolysis, as long as the degree of hydrolysis of the PVA resin is within the ranges described herein. Optionally, the PVA resin can, in addition or in the alternative, include a first PVA polymer that has a Mw in a range of about 50,000 to about 300,000 Daltons, or about 60,000 to about 150,000 Daltons; and a second PVA polymer that has a Mw in a range of about 60,000 to about 300,000 Daltons, or about 80,000 to about 250,000 Daltons. Of the total PVA resin content in the film described herein, the PVA resin can comprise about 30 to about 85 wt% of the first PVA polymer, or about 45 to about 55 wt% of the first PVA polymer. For example, the PVA resin can contain about 50 w.% of each PVA polymer, wherein the viscosity of the first PVA polymer is about 13 cP and the viscosity of the second PVA polymer is about 23 cP.

**[0043]** The films may be water soluble copolymer films comprising a least one negatively modified monomer with the following formula:



wherein Y represents a vinyl alcohol monomer and G represents a monomer comprising an anionic group and the index n is an integer of from 1 to 3. G can be any suitable comonomer capable of carrying of carrying the anionic group, for example G is a carboxylic acid. G may be selected from the group consisting of maleic acid, itaconic acid, coAMPS, acrylic acid, vinyl acetic acid, vinyl sulfonic acid, allyl sulfonic acid, ethylene sulfonic acid, 2 acrylamido 1 methyl propane sulfonic acid, 2 acrylamido 2 methyl propane sulfonic acid, 2 methyl acrylamido 2 methyl propane sulfonic acid, and mixtures thereof. Suitable films may include blends of such copolymers.

**[0044]** The anionic group of G may be preferably selected from the group consisting of  $\text{OSO}_3\text{M}$ ,  $\text{SO}_3\text{M}$ ,  $\text{CO}_2\text{M}$ ,  $\text{OCO}_2\text{M}$ ,  $\text{OPO}_3\text{M}_2$ ,  $\text{OPO}_3\text{HM}$  and  $\text{OPO}_2\text{M}$ . More preferably, the anionic group of G is selected from the group consisting of  $\text{OSO}_3\text{M}$ ,  $\text{SO}_3\text{M}$ ,  $\text{CO}_2\text{M}$ , and  $\text{OCO}_2\text{M}$ . Most preferably the anionic group of G is selected from the group consisting of  $\text{SO}_3\text{M}$  and  $\text{CO}_2\text{M}$ . As used herein, M is a suitable counterion known to one of ordinary skill, such as hydrogen ( $\text{H}^+$ ), an alkali metal (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ), an alkali earth metal ( $1/2 \text{Ca}^{2+}$ ), or ammonium ( $\text{NH}_4^+$ ).

**[0045]** The film material for the first layer herein can also comprise one or more additive ingredients. For example, the film preferably comprises a plasticizing agent. The plasticizing agent may comprise water, glycerol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, sorbitol, or mixtures thereof. In some aspects, the film comprises from about 2% to about 35%, or from about 5% to about 25%, by weight of the film, a plasticizing agent selected from group comprising water, glycerol, diethylene glycol, sorbitol, and mixtures thereof. In some aspects, the film material comprises at least two, or preferably at least three, plasticizing agents. In some aspects, the film is substantially free of ethanol, meaning that the film comprises from 0% (including 0%) to about 0.1% ethanol by weight of the film. In some aspects, the plasticizing agents are the same as solvents found in an encapsulated liquid composition.

**[0046]** Other additives may include water and functional detergent additives, including surfactant, to be delivered to the wash water, for example, organic polymeric dispersants, etc. Additionally, the film may comprise an aversive agent, further described herein.

**[0047]** Preferably, the first layer comprises less than  $200 \text{ mg/m}^2$ , preferably less than  $50 \text{ mg/m}^2$ , even more preferably less than  $10 \text{ mg/m}^2$ , most preferably less than  $1 \text{ mg/m}^2$  of aversive agent. The first layer maybe substantial devoid of aversive agent. By 'substantially devoid' we herein mean no aversive agent has intentionally been added to the first layer.

**[0048]** One embodiment of the present invention is a water-soluble unit dose article comprising a detergent or cleaning composition, a water-soluble film, wherein the water-soluble film comprises at least a first layer, an aversive agent and wherein said water-soluble film exhibits at least a 50% aversive retention of at least 2 weeks, preferably at least 4 weeks, more preferably at least 1 month, most preferably at least 2 months. By 'aversive retention' we herein mean at least 50% of the initial concentration of aversive agent added to the water-soluble film remains in the water-soluble film after at least 2 weeks, preferably at least 4 weeks, more preferably at least 1 month, most preferably at least 2 months.

**[0049]** Suitable water-soluble films to achieve this are described in the section titled 'first layer'. The detergent or cleaning composition is as described in the section titled 'detergent or cleaning composition'. The aversive agent may be located on the outside of the unit dose article, in other words on the outer surface of the water-soluble film, or may be located within the water-soluble film. Suitable aversive agents are described in the section titled 'aversive agent'.

**[0050]** The aversive agent in this embodiment may be formulated into the water-soluble film ahead of manufacturing the unit dose article, may be added to the outside of the water-soluble film ahead of formation into the unit dose article, or maybe added to the outside of the unit dose article post manufacture of the unit dose article.

Second layer

**[0051]** The second layer comprises an aversive agent. The second layer may comprise between 5mg/m<sup>2</sup> and 500mg/m<sup>2</sup>, preferably between 20mg/m<sup>2</sup> and 200mg/m<sup>2</sup> of the water-soluble film of the aversive agent. The aversive agent is described below.

**[0052]** The aversive agent is formulated within the second layer, such that it is dispersed within the second layer. The second layer may comprise regions of higher concentration of aversive agent, or the aversive agent may be homogeneously dispersed within the second layer.

**[0053]** The second layer may be non-fibrous, fibrous or a mixture thereof. Preferably the second layer has a different composition to the first layer but may comprise one or more of the same ingredients.

**[0054]** The second layer may be non-fibrous and is preferably selected from polymeric film material, a gel, a resin or mixtures thereof.

**[0055]** The second layer may comprise a polymeric material as described for the first layer.

**[0056]** Preferably, the second layer comprises gums, carbohydrates, celluloses, lipids, proteins or mixtures thereof.

**[0057]** The second layer may comprise gum arabic, sodium alginate, carrageenan, starch, dextran, sucrose, carboxymethyl cellulose, methyl cellulose, wax, stearic acid, phospholipids, gelatin, albumin or mixtures thereof.

**[0058]** The second layer may be in the form of a gel matrix comprising the aversive agent. A gel in this case means a composition of sufficiently high viscosity such that it substantially remains adhered to the first layer until intended use. The gel matrix may comprise a wax, a saccharide, or a mixture thereof.

**[0059]** Preferably the second layer is one that exhibits at least a 50% aversive retention of at least 2 weeks, preferably at least 4 weeks, more preferably at least 1 month, most preferably at least 2 months. By 'aversive retention' we herein mean at least 50% of the initial concentration of aversive agent added to the second layer remains in the second layer after at least 2 weeks, preferably at least 4 weeks, more preferably at least 1 month, most preferably at least 2 months.

**[0060]** The second layer may be applied to the first layer during casting of the first layer, thermoforming of the unit dose article or a mixture thereof. Alternatively, the second layer may be applied to the first layer via spraying, printing, electrostatic transfer and mixtures thereof. Suitable printing techniques include, flexographic printing, lithographic printing, gravure printing, ink jet printing, laser printing or mixtures thereof.

Aversive agent

**[0061]** As used herein, an aversive agent is an agent that is intended to discourage ingestion and/or consumption of the unit dose articles described herein or components thereof, such as water-soluble films. An aversive agent may act by providing an unpleasant sensation, such as an unpleasant taste, when placed in the mouth or ingested. Such unpleasant sensations may include bitterness, pungency (or heat/spiciness), an unpleasant odor, sourness, coldness, and combinations thereof. An aversive agent may also act by causing humans and/or animals to vomit, for example via emetic agents. Suitable aversive agents include bittering agents, pungent agents, emetic agents, and mixtures thereof.

**[0062]** The level of aversive agent used within or on the unit dose articles or components thereof may be at least at an effective level, which causes the desired aversive effect, and may depend on the characteristics of the specific aversive agents, for example bitter value. The level used may also be at or below such a level that does not cause undesired transfer of the aversive agents to a human and/or animal, such as transfer to hands, eyes, skin, or other body parts. The amount present may be based on the particular aversive agent's potency such that greater than 50% of humans experience an aversive effect when exposed to the given amount of the aversive agent. The aversive agent may be present at a concentration which elicits repulsive behavior within a maximum time of six seconds in cases of oral exposure.

**[0063]** The aversive agent may be provided to the second layer in any suitable manner. The aversive agent may be formulated into a film-forming material during manufacture of the second layer, or it may be provided after the film is manufactured, or even during or after the manufacture of the unit dose article. If the aversive agent is formulated into the second layer of the water-soluble film as the film is being manufactured, the water-soluble film may comprise a substrate element and an aversive agent chemically coupled to the substrate element, for example as described in US2014/0371411A1. The aversive agent may be provided in compositions encapsulated by water-soluble film, and may migrate to the film and/or to the surface of the film, which may be facilitated by the selection of certain solvents and/or plasticizers.

**[0064]** The aversive agent may be provided in any suitable form. The aversive agent may be in the form of particles comprising the aversive agent, encapsulates comprising the aversive agent, a gel matrix comprising the aversive agent, or a combination thereof. In such forms, the aversive agent may be held within or on the carrier, within the encapsulate, and/or within the gel matrix until it is contacted with a relevant substrate, such as saliva, after which the aversive agent is released.

**[0065]** The aversive agent may be in the form of particles comprising a carrier and the aversive agent. The carrier

maybe selected from the group comprising carbonate, sulphate, zeolite, talc, clay, saccharides, polysaccharides, or mixtures thereof. The carrier may comprise a polysaccharide, which may be selected from maltodextrin, cellulose or a mixture thereof.

**[0066]** The carrier may form a matrix into which the aversive agent is absorbed. The aversive agent may be coated onto the carrier. The carrier may form a matrix into which the aversive agent is absorbed and the aversive agent is coated onto the carrier. For example, the aversive agent may be coated onto the carrier and then at least part of the aversive agent is absorbed into the carrier.

**[0067]** Wherein the aversive agent is in the form of a particle, the particle may be a spray-dry particle, an agglomerate, an extrudate, or a mixture thereof.

**[0068]** When the aversive agent is in the form of an encapsulate, the encapsulate maybe a core and shell encapsulate, where the core comprises the aversive agent. The shell may comprise polyvinyl alcohol, melamine formaldehyde, polylactide, polyglycolide, gelatin, polyacrylate, shellac, zein, chitosan, wax, hydrogenated vegetable oil, polysaccharides paraffin and mixtures thereof. The shell may comprise a polylactide-polyglycolide copolymer. The shell may comprise a hydrogenated castor oil.

**[0069]** The aversive agent may be selected from the group comprising naringin; sucrose octaacetate; denatonium benzoate; capsinoids (including capsaicin); vanillyl ethyl ether; vanillyl propyl ether; vanillyl butyl ether; vanillin propylene; glycol acetal; ethylvanillin propylene glycol acetal; gingerol; 4-(1-menthoxymethyl)-2-(3'-methoxy-4'-hydroxy-phenyl)-1, 3-dioxolane; pepper oil; pepperoleoresin; gingeroleoresin; nonylic acid vanillylamide; jamboo oleoresin; Zanthoxylum piperitum peel extract; sanshool; sanshoamide; black pepper extract; chavicine; piperine; spilanthol; and mixtures thereof. Other suitable aversive agents are described in more detail below.

**[0070]** The aversive agent may comprise a bittering agent.

**[0071]** Non-limiting examples of suitable bittering agents include denatonium salts and derivatives thereof. The bittering agent may be a denatonium salt selected from the group consisting of denatonium chloride, denatonium citrate, denatonium saccharide, denatonium carbonate, denatonium acetate, denatonium benzoate, and mixtures thereof. The bittering agent may be denatonium benzoate, also known as phenylmethyl-[2- [(2,6-dimethylphenyl)amino]- 2-oxoethyl]-diethylammonium benzoate, CAS no. 3734-33-6. Denatonium benzoate is commercially sold as BITREX®, available from Macfarlan Smith, Edinburgh, Scotland, UK.

**[0072]** The bittering agent may be a natural bitter substance. The natural bitter substance may be selected from the group consisting of glycosides, isoprenoids, alkaloids, amino acids, and mixtures thereof. For example, suitable bittering agents also include Quercetin (3,3',4',5,7-pentahydroxyflavone); Naringin (4',5,7-Trihydroxyflavanone-7-rhamnoglucoside); Aucubin; Amarogentin; Dihydrofoliamentin; Gentiopicroside; Gentiopicroin; Swertiamarin; Swerosid; Gentioflavosid; Centaurososid; Methiafolin; Harpagoside; Centapikrin; Saillcin; Kondurangin; Absinthin; Artabsin; Cnicin; Lactucin; Lactucopicroin; Salontenolid;  $\alpha$ -thujone;  $\beta$ -thujone; Desoxy Limonene; Limonin; Ichangin; iso-Obacunoic Acid; Obacunone; Obacunoic Acid; Nomilin; Ichangin; Nomilinoic acid; Marrubin; Pramarrubin; Carnosol; Carnosic acid; Quassin; Brucine; Quinine hydrochloride; Quinine sulfate; Quinine dihydrochloride; Columbine; Caffeine; Threonine; Methionine; Phenylalanine; Tryptophan; Arginine; Histidine; Valine; Aspartic acid; Sucrose octaacetate; and mixtures thereof. Other suitable bittering agents include quinine bisulfate and hop extract (e.g., humulone).

**[0073]** Other non-limiting examples of suitable bittering agents for use as described herein are described at BitterDB (<http://bitterdb.agri.huji.ac.il/dbbitter.php>), which is a free searchable database of bittering agents that holds over 680 bittering agents obtained from literature and the Merck Index and their associated 25 human bitter taste receptors (hT2Rs), and in the corresponding paper Ayana Wiener; Marina Shudler; Anat Levit; Masha Y. Niv. BitterDB: a database of bitter compounds. Nucleic Acids Res 2012, 40(Database issue): D413-419.

**[0074]** The bittering agent may exhibit a bitter value of greater than 1,000, or greater than 5,000, or greater than 10,000, or greater than 20,000, and/or less than 10,000,000, or less than 5,000,000, or less than 1,000,000, or less than 500,000, or less than 200,000, or less than 150,000, or less than 100,000. The bittering agent may exhibit a bitter value of from about 1,000 to about 10,000,000, or from about 5,000 to about 1,000,000, or from about 10,000 to about 200,000. The bitter value is measured using the standardized process set forth in the European Pharmacopoeia (5th Edition, Stuttgart 2005, Volume 1, General Monograph Groups, 2.8.15 Bitterness Value, p. 278).

**[0075]** The aversive agent may comprise a pungent agent. Pungent agents provide pungency, which is the characteristic commonly referred to as spiciness, hotness, or "heat," often found in foods such as chili peppers.

**[0076]** Non-limiting examples of suitable pungent agents may include: capsinoids (including capsaicin); vanillyl ethyl ether; vanillyl propyl ether; vanillyl butyl ether; vanillin propylene; glycol acetal; ethylvanillin propylene glycol acetal; capsaicin; gingerol; 4-(1-menthoxymethyl)-2-(3'-methoxy-4'-hydroxy-phenyl)-1, 3-dioxolane; pepper oil; pepper oleoresin; ginger oleoresin; nonylic acid vanillylamide; jamboo oleoresin; Zanthoxylum piperitum peel extract; sanshool; sanshoamide; black pepper extract; chavicine; piperine; spilanthol; and mixtures thereof. Other suitable pungent agents include polygodial, Tasmannia lanceolata extract, Capsicum extracts, or mixtures thereof. The pungent agent may comprise a capsaicinoid, for example capsaicin, dihydrocapsaicin, nordihydrocapsaicin, homodihydrocapsaicin, homocapsaicin, and/or nonivamide. The pungent agent may comprise capsaicin.



**[0077]** Commercially available suitable pungent agents include OPTAHEAT (Symise Flavors), HOTACT (Lipo Chemicals), and HEATENOL (Sensient Flavors).

**[0078]** The unit dose article and/or component thereof (e.g., water-soluble film) may comprise a sufficient amount of the pungent agent to deliver a pungent taste and/or pungent smell, for example a controlled level of pungency to a user (enough to deter ingestion but not so much as to make a human and/or animal physically ill or to accidentally transfer significant amounts to a user's hands).

**[0079]** The pungency of a pungent agent may be determined according to the well-known Scoville Scale and may be reported in Scoville heat units (SHU). The pungent agent may be selected from pungent agents having a pungency level of at least about 1,000,000 SHU, or at least about 5,000,000 SHU, or at least about 10,000,000 SHU, or at least about 15,000,000 SHU. For comparison, the pungency level of capsaicin is about 16,000,000 SHU. Pungency may also be measured by high performance liquid chromatography and determined in American Spice Trade Association (ASTA) pungency units. A measurement of one part capsaicin per million corresponds to about 15 Scoville units, and ASTA pungency units can be multiplied by 15 and reported as Scoville units.

**[0080]** Because it is desirable that the pungent agent be detectable in order to be an effective aversive agent, it is generally desirable that the pungency not be masked by other agents, such as cooling agents like menthol and the like. Therefore, the unit dose articles and/or components thereof maybe free, for example comprising less than 5%, or less than 3%, or less than 1%, or less than 0.1%, or less than 0.01%, or less than 0.001%, or about 0%, or 0%, by weight of the article or component, of cooling agents, for example menthol and/or eucalyptus.

**[0081]** The aversive agent may comprise an emetic agent. There are two main types of emetic agents: 1) those that work directly on the gastrointestinal tract of humans and animals, and 2) those that work indirectly by stimulating the areas of the brain that control vomiting.

**[0082]** Non-limiting examples of suitable emetic agents that work directly on the gastrointestinal tracts are selected from the group consisting of: ipecac (ipecac syrup and/or ipecac powder) obtained from *Cephaelis ipecacuanha*, lobelia obtained from *Lobelia inflata*, mustard seed obtained from *Brassica juncea*, vomitoxin obtained from *Fusarium graminearum*, copper sulfate, and mixtures thereof. The aversive agent may comprise ipecac.

**[0083]** An example of an emetic agent that works indirectly by stimulating the areas of the brain that control vomiting is apomorphine (apomorphine hydrochloride).

**[0084]** To determine the presence and/or amount of aversive agent present on the surface of the film, sensory or analytical techniques may be employed. A suitable sensory technique (e.g., via taste in controlled circumstances) is disclosed in WO2014/026855 A1, assigned to Henkel AG & Co.

**[0085]** The aversive agent may be extracted from the surface via the following method. The unit dose pouch is held with tweezers at the seal. The surface of the each side of the pouch is rinsed 10 times, with 4 to 5 mL of methanol used in each rinse cycle and collected. After rinsing, the methanol solution is transferred to a glass vial, and the methanol is evaporated. The remaining extract is then dissolved in the appropriate solvent needed for the analytical method.

**[0086]** Aversive agents can be assayed via standard methods known to those skilled in the art. Analytical techniques may include chromatography or spectroscopic techniques known to one skilled in the art. For example, suitable methods are disclosed in Falkner et al., Journal of Chromatography A. 715 (1995) 189-194, and in R. Bucci et al., Talanta 68 (2006) 781-790.

#### Detergent or cleaning composition

**[0087]** The water-soluble unit dose article comprises a detergent or cleaning composition. The detergent or cleaning composition may be a fabric detergent or cleaning composition, an automatic dishwashing detergent or cleaning composition or a mixture thereof.

**[0088]** By 'fabric detergent or cleaning composition' we herein mean compositions that provide cleaning benefit to fabrics, care benefit to fabrics or a mixture thereof.

**[0089]** The fabric detergent or cleaning composition may provide a cleaning benefit selected from stain removal, stain-repellency, anti-soil-redeposition, brightening, whitening dirt removal, malodour reduction or mixtures thereof.

**[0090]** The fabric detergent or cleaning composition may provide a care benefit selected from softening, freshness, anti-wrinkling, anti-colour fading, dye transfer inhibition, anti-static or mixtures thereof.

**[0091]** By 'automatic dishwashing detergent or cleaning composition' we herein mean automatic dishwashing compositions that provide cleaning benefits, care benefits or a mixture thereof. "Automatic dishwashing care benefits" refers to any automatic dishwashing composition that can provide shine, fast drying, metal, glass or plastic protection benefits.

**[0092]** The detergent or cleaning composition maybe in the form of a powder, a compacted powder, a liquid, or a mixture thereof.

**[0093]** By 'liquid' we herein mean any composition capable of wetting and treating a substrate and encompasses forms such as dispersions, gels, pastes and the like. A dispersion, for example, is a liquid comprising solid or particulate matter contained therein. The liquid composition may also include gases in suitably subdivided form.

**[0094]** The cleaning composition may comprise anionic surfactants, non-ionic surfactants, cationic surfactants, polyethylene glycol polymers, ethoxylated polyethyleneimines, rheology modifier, hueing dyes, perfumes, perfume microcapsules, chelants, enzymes, silicones, polyolefin waxes, latexes, oily sugar derivatives, cationic polysaccharides, polyurethanes, fatty acids, enzyme stabilizing systems; antioxidants, opacifier, pearlescent agent, deposition aid, builder, bleaching agent, bleach activator, bleach catalyst, organic shine polymers, surface modifying polymers, metal care agents, metal salts, anti-corrosion agents and mixtures thereof.

**[0095]** The detergent or cleaning composition may comprises from about 1% to 80% by weight of the detergent or cleaning composition of a surfactant. The surfactant may comprise anionic, nonionic, zwitterionic, ampholytic, zwitterionic, semi-polar, cationic surfactants or mixtures thereof. The surfactant may comprise anionic, nonionic, cationic surfactants and mixtures thereof.

**[0096]** The detergent or cleaning composition may comprise an enzyme. The enzyme may be selected from hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, and amylases, or mixtures thereof.

**[0097]** The detergent or cleaning composition may comprise a polymer. The polymer may be selected from carboxylate polymers, polyethylene glycol polymers, terephthalate polymers, amine polymers, cellulosic polymers, dye transfer inhibition polymers, dye lock polymers such as a condensation oligomer produced by condensation of imidazole and epichlorhydrin, optionally in ratio of 1:4:1, hexamethylenediamine derivative polymers, ethoxylated polyethyleneimines and any combination thereof.

**[0098]** Other polymers include hydroxyethyl cellulose polymer. Preferably, the hydroxyethyl cellulose polymer is derivatised with trimethyl ammonium substituted epoxide. The cellulose polymer may have a molecular weight of between 100,000 and 800,000 daltons. The hydroxyethyl cellulose polymer may be added to the composition as a particle. It may be present in the composition of the particle or maybe also be present as a liquid, or a mixture thereof.

**[0099]** The detergent or cleaning composition may comprise a rheology modifier. The rheology modifier can be selected from the group consisting of non-polymeric crystalline hydroxyfunctional materials, polymeric rheology modifiers or mixtures thereof. Specific examples of suitable crystalline, hydroxyl-containing rheology modifiers include castor oil and its derivatives. Also practical are hydrogenated castor oil derivatives such as hydrogenated castor oil and hydrogenated castor wax.

**[0100]** The detergent or cleaning composition may comprise a builder. Suitable builders include polycarboxylate builders include cyclic compounds, particularly alicyclic compounds. Particularly suitable are citrate builders, e.g., citric acid and soluble salts thereof, particularly sodium salts thereof. The builder may be selected from aminocarboxylate builders, preferably selected from salts of MGDA (methyl-glycine-diacetic acid), GLDA (glutamic-N,N- diacetic acid), EDDS (ethylene diamine disuccinates) iminodisuccinic acid (IDS) and carboxymethyl inulin.

**[0101]** The detergent or cleaning composition may comprise a bleaching agent. Bleaching agents may comprise chlorine bleaches, oxygen bleaches, or mixtures thereof. Preferably, the bleach is selected from sodium perborate monohydrate, sodium perborate tetrahydrates, sodium percarbonate and mixtures thereof.

**[0102]** The detergent or cleaning composition may comprise a peroxyacid bleach precursors, preferably selected from precursors of perbenzoic acid, cationic peroxyacid precursors, peracetic acid, sodium acetoxylbenzene sulfonate, pentaacetylglucose, sodium 3,5,5-trimethylhexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), amide substituted alkyl peroxyacid precursors, benzoxazin peroxyacid precursors and mixtures thereof. The bleach may comprise  $\epsilon$ -phthalimidoperoxyacaproic acid[phthalimidoperoxyhexanoic acid (PAP).

**[0103]** Preferably, if the detergent or cleaning composition comprises an automatic dish washing composition, the automatic dishwashing composition is phosphate free, or substantially phosphate free.

**[0104]** The detergent or cleaning composition may comprise a hueing dye, a brightener or a mixture thereof.

**[0105]** Preferably the detergent or cleaning composition comprises a non-aqueous solvent, preferably between 5% and 30%, more preferably between 7% and 25% by weight of the detergent or cleaning composition of a non-aqueous solvent. Preferably, the non-aqueous solvent is selected from glycerol, ethylene glycol, 1,3 propanediol, 1,2 propanediol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, 2,3-butane diol, 1,3 butanediol, diethylene glycol, triethylene glycol, polyethylene glycol, glycerol formal dipropylene glycol, polypropylene glycol, dipropylene glycol n-butyl ether, and mixtures thereof.

**[0106]** The detergent or cleaning composition may comprise water, preferably from 0.1% to 20%, more preferably from 0.5% to 15%, most preferably from 1% to 13.5% by weight of the detergent or cleaning composition of water.

#### Process for Making

**[0107]** The present invention is also to a process for making a water-soluble unit dose article according to the present invention comprising the steps of;

- a. Preparing a first layer of a water-soluble film wherein the first layer comprises polyvinyl alcohol;
- b. Preparing a second layer of a water-soluble film wherein the second layer comprises an aversive agent;
- c. Combining the first and second layers to form the water-soluble film;
- d. Preparing a water-soluble unit dose article comprising the film of part c.

**[0108]** The present invention is also to a process for making a water-soluble unit dose article according to the present invention comprising the steps of;

- a. Preparing a first layer of a water-soluble film wherein the first layer comprises polyvinyl alcohol;
- b. Adding a second layer onto the first layer, wherein the second layer comprises an aversive agent by adding the second layer via coating, spraying, printing, electrostatic transfer and mixtures thereof to form the water-soluble film;
- c. Preparing a water-soluble unit dose article comprising the film of part b.

**[0109]** The present invention is also to a process for making a water-soluble unit dose article according to the present invention comprising the steps of;

- a. Preparing a water-soluble unit dose article comprising a film having a first layer, wherein the first layer comprises polyvinyl alcohol;
- b. Adding a second layer onto the first layer, wherein the second layer comprises an aversive agent by adding the second layer via coating, spraying, printing, electrostatic transfer and mixtures thereof.

**[0110]** The second layer may be applied to the first layer during casting of the first layer, thermoforming of the unit dose article or a mixture thereof. The second layer may be applied to the first layer via spraying, printing, electrostatic transfer and mixtures thereof. Suitable printing techniques include, flexographic printing, lithographic printing, gravure printing, ink jet printing, laser printing or mixtures thereof.

#### Method of use

**[0111]** The present invention is also to a method of doing laundry comprising the steps of diluting a water-soluble unit dose article according to the present invention in water by a factor of at least 400 to form a wash liquor and then washing fabrics with said wash liquor.

**[0112]** The unit dose article of the present invention may be used alone in the wash operation or may be used in conjunction with other laundry additives such as fabric softeners or fabric stain removers. The unit dose article may be used in conjunction with fragrance boosting compositions such as commercially available 'Lenor Unstoppables'.

**[0113]** The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

#### EXAMPLES

##### Example 1

**[0114]** An aversive agent was coated onto a water-soluble film. The water-soluble film was formed into a water-soluble unit dose article. The composition within the water-soluble unit dose article was the same as found in unit dose articles as found in a packaged product commercially available from UK supermarkets under the brand Ariel 3in1 Pods.

##### Example 2

**[0115]** Fig. 1 shows a side profile cross section of a water-soluble unit dose article (1) comprising a film (2) having a first layer (3) and a second layer (4), wherein the second layer (4) comprises an aversive agent. In this example the second layer (4) is present over the entire surface of the first layer (3).

**[0116]** Fig.2 shows a unit dose article (1) comprising a film (2) having a first layer (3) and a second layer (4) wherein the second layer (4) is present as a discrete region on the surface of the first layer (3) and wherein the second layer (4) comprises an aversive agent.

## Claims

1. A water-soluble unit dose article comprising a detergent or cleaning composition, a water-soluble film, wherein the water-soluble film comprises a first layer and a second layer wherein the first and second layers are in contact, wherein the first layer comprises a polymeric material and the second layer comprises an aversive agent.
2. The water-soluble unit dose article according to claim 1, wherein the water-soluble film comprises between 5mg/m<sup>2</sup> and 500mg/m<sup>2</sup>, preferably between 20mg/m<sup>2</sup> and 200mg/m<sup>2</sup> of the water-soluble film of the aversive agent.
3. The water-soluble unit dose article according to claim 2, wherein the second layer comprises between 5mg/m<sup>2</sup> and 500mg/m<sup>2</sup>, preferably between 20mg/m<sup>2</sup> and 200mg/m<sup>2</sup> of the water-soluble film of the aversive agent.
4. The water-soluble unit dose article according to any preceding claims, wherein the first layer has an inner surface and an outer surface, and wherein the second layer is in contact with at least a portion a surface of the first layer, or is in contact with an entire surface of the first layer, preferably wherein the second layer is in contact with at least a portion of the outer surface of the first layer or the entire outer surface of the first layer.
5. The water-soluble unit dose article according to claim 3, wherein the second layer is in contact with between 5% and 100%, preferably between 10% and 95%, more preferably between 15% and 90% of the surface area of either the inner surface or the outer surface of the first layer.
6. The water-soluble unit dose article according to any preceding claims wherein the polymeric material of the first layer comprises polyvinyl alcohol, polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids or salts, polyaminoacids, peptides, polyamides, polyacrylamide, copolymers of maleic/acrylic acids, polysaccharides, natural gums or a mixture thereof.
7. The water-soluble unit dose article according to any preceding claims wherein the second layer is a non-fibrous, a fibrous or a mixture thereof.
8. The water-soluble unit dose article according to claim 6 wherein the second layer is non-fibrous and is preferably selected from polymeric film material, a gel, a resin or mixtures thereof.
9. The water-soluble unit dose article according to any preceding claims wherein the second layer comprises gums, carbohydrates, celluloses, lipids, proteins or mixtures thereof.
10. The water-soluble unit dose article according to any preceding claims, wherein the first layer, the second layer, or both exhibits at least a 50% aversive retention of at least 2 weeks, preferably at least 4 weeks, more preferably at least 1 month, most preferably at least 2 months..
11. The water-soluble unit dose article according to any preceding claims wherein the aversive agent is selected from the group comprising naringin; sucrose octaacetate; denatonium benzoate; capsinoids (including capsaicin); vanillyl ethyl ether; vanillyl propyl ether; vanillyl butyl ether; vanillin propylene; glycol acetal; ethylvanillin propylene glycol acetal; capsaicin; gingerol; 4-(1-menthoxymethyl)-2-(3'-methoxy-4'-hydroxy-phenyl)-1,3-dioxolane; pepper oil; pepperoleoresin; gingeroleoresin; nonylic acid vanillylamide; jamboo oleoresin; Zanthoxylum piperitum peel extract; sanshool; sanshoamide; black pepper extract; chavicine; piperine; spilanthol; and mixtures thereof.
12. The water-soluble unit dose article according to any preceding claims wherein the detergent or cleaning composition comprises a substrate treatment agent and wherein the substrate treatment agent is preferably selected from the group comprising anionic surfactants, non-ionic surfactants, cationic surfactants, polyethylene glycol polymers, ethoxylated polyethyleneimines, rheology modifier, hueing dyes, perfumes, perfume microcapsules, chelants, enzymes, silicones, polyolefin waxes, latexes, oily sugar derivatives, cationic polysaccharides, polyurethanes, fatty acids, enzyme stabilizing systems; antioxidants, opacifier, pearlescent agent, deposition aid, builder, bleaching agent, bleach activator, bleach catalyst, organic shine polymers, surface modifying polymers, metal care agents, metal salts, anti-corrosion agents and mixtures thereof.
13. The water-soluble unit dose article according to any preceding claims wherein the detergent or cleaning composition comprises a non-aqueous solvent, preferably selected from glycerol, ethylene glycol, 1,3 propanediol, 1,2 propan-

ediol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, 2,3-butane diol, 1,3 butanediol, diethylene glycol, triethylene glycol, polyethylene glycol, glycerol formal dipropylene glycol, polypropylene glycol, dipropylene glycol n-butyl ether, and mixtures thereof.

5     **14.** The water-soluble unit dose article according to any preceding claims wherein the unit dose article comprises at least two internal compartments, or even at least three compartments or even at least four compartments.

**15.** A process for making a water-soluble unit dose article according to any preceding claims comprising the steps of;

- 10             a. Preparing a first layer of a water-soluble film wherein the first layer comprises polyvinyl alcohol;  
               b. Preparing a second layer of a water-soluble film wherein the second layer comprises an aversive agent;  
               c. Combining the first and second layers to form the water-soluble film;  
               d. Preparing a water-soluble unit dose article comprising the film of part c.

15     **16.** A process for making a water-soluble unit dose article according to any preceding claims comprising the steps of;

- a. Preparing a first layer of a water-soluble film wherein the first layer comprises polyvinyl alcohol;  
               b. Adding a second layer onto the first layer, wherein the second layer comprises an aversive agent, by adding the second layer via coating, spraying, printing, electrostatic transfer and mixtures thereof to form the water-soluble film;  
 20             c. Preparing a water-soluble unit dose article comprising the film of part b.

**17.** A process for making a water-soluble unit dose article according to any preceding claims comprising the steps of;

- 25             a. Preparing a water-soluble unit dose article comprising a film having a first layer, wherein the first layer comprises polyvinyl alcohol;  
               b. Adding a second layer onto the first layer, wherein the second layer comprises an aversive agent by adding the second layer via coating, spraying, printing, electrostatic transfer and mixtures thereof.

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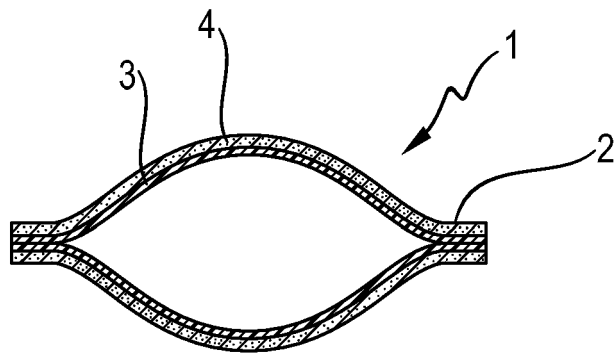
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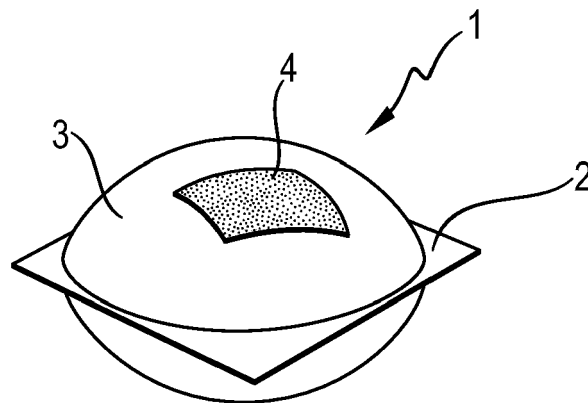
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**Fig. 1**



**Fig. 2**





## EUROPEAN SEARCH REPORT

Application Number  
EP 16 17 5442

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2015/158646 A1 (MEIER FRANK [DE] ET AL) 11 June 2015 (2015-06-11)	1-14	INV. C11D17/04 B65D65/46
A	* examples V1,V2 * * paragraphs [0011], [0008], [0028], [0046] - [0049] *	15-17	
Y	----- EP 1 375 377 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]) 2 January 2004 (2004-01-02) * paragraphs [0051], [0039] - [0050] *	1-17	
Y	----- US 5 783 541 A (TACK JORIS JOSEF GUSTAAF [IT] ET AL) 21 July 1998 (1998-07-21) * column 4, line 26 - line 33 * * column 5, line 2 - line 7 * -----	1-17	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
			C11D B65D
Place of search		Date of completion of the search	Examiner
Munich		12 January 2017	Culmann, J
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